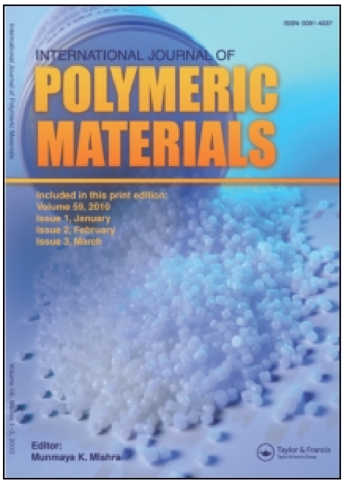

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Kajiyama, Tisato and Takahara, Atsushi(2000) 'Physical Properties of Polymeric Solids', International Journal of Polymeric Materials, 46: 1, 227 — 231

To link to this Article: DOI: 10.1080/00914030008054856

URL: http://dx.doi.org/10.1080/00914030008054856

Intern. J. Polymeric Mater., 2000, Vol. 46, pp. 227–231
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Physical Properties of Polymeric Solids

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(Received 25 September 1998)

Progress in physical properties of polymeric solids in Japan is reviewed.

Keywords: Thermal properties; molecular motion; dynamic viscoelasticity; scanning viscoelasticity microscopy; dielectric property; block copolymer; high-strength fibers

1. THERMAL PROPERTIES

Various methods for the characterization of thermal properties of polymers have been developed recently. Y. Saruyama (3881) studied a melting transition of polymer crystals by light-modulated calorimetry [1]. The light-modulated differential scanning calorimeter (or light-heating dynamic DSC) was constructed to give heat-flow modulation to the sample by using heat generated upon light irradiation. A frequency dependence of the complex heat capacity was measured in a 0.01–0.2 Hz range. In a melting temperature range, the real part of the complex heat capacity at a frequency range above 0.1 Hz reached the constant value. Low signal to noise ratios in the modulation amplitude and the phase were realized by the higher modulation frequency than that the commercially available light modulated DSC.

T. Hashimoto, C. Sawatari *et al.* (3889) developed a novel temperature wave analysis (TWA) that made it possible to obtain the frequency dependent thermal diffusivity as a function of temperature [2]. The

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thermal diffusivity of materials in solid and liquid states, except for electrical conductors, can be measured in the frequency range from 10 Hz to 2 kHz. Therefore, this technique enables measurements of frequency dependent thermal diffusivity at the glass transition, the melting and the crystallization temperatures of polymers. The thermal diffusivity of ultradrawn high molecular weight polyethylene (UHMWPE) films with various draw ratios was measured in a temperature range from room temperature to above the melting point under a constant heating or cooling process. The thermal diffusivity along the direction normal to the drawing direction decreased with an increase in draw ratio. The onset of changes in thermal diffusivity shifted to a higher temperature side with an increase of draw ratio.

2. VISCOELASTICITY AND MOLECULAR MOTION

T. Yamamoto, K. Nozaki (2879) investigated an interdiffusion process of *n*-alkane molecules in a crystal phase and also, the temperature dependence of the diffusivity based on *in situ* optical microscopy [3]. The optical observation of the molecular interdiffusion is possible owing to the mixing-induced solid state transition to the rotator phase of *n*-alkane. A molecularly mixed region and a low-temperature phase matrix form a sharp interphase boundary which is visible under the polarized microscope. A diffusion couple by a mechanical junction of single-crystalline $C_{23}H_{48}$ and polycrystalline $C_{21}H_{44}$ was prepared. The chain diffusivity at each temperature was determined from the microscopically determined advance of the interphase boundary. The diffusivity showed a remarkable temperature dependence in a temperature range from 304 to 312 K. The interdiffusion was rather active above 306 K but it became remarkably inactive below 306 K. An apparent activation energy for the interdiffusion above 306 K was estimated to be about 300 kJ mol^{-1}. The mechanism of the interphase-boundary motion was discussed on the basis of the formulation derived for the moving boundary problem of diffusion (the Stefan problem).

Scanning force microscopy can be used for the measurement of surface molecular motion of polymeric solids [4, 5]. T. Kajiyama, A. Takahara *et al.* (3629) carried out lateral force microscopic (LFM) measurements of monodisperse polystyrene (PS) films with number-average molecular weights (Mns) of 4.9 k and 140 k at various temperatures in order to investigate the surface relaxation process. It was revealed that the surface *Tg* of the monodisperse PS film was lower than the bulk one, even though Mn was fairly large as 140 k. The time-temperature superposition was applicable to the surface primary relaxation process [3] and the master curve of lateral force *vs.* scanning rate was constructed. The activation energy for the surface micro-Brownian segmental motion (surface glass transition) was evaluated from the temperature dependence of shift factor to be $220-250\,\mathrm{kJ{\cdot}mol^{-1}}$. This value is almost half as large as that for the bulk micro-Brownian motion of PS.

K. Nitta *et al.* (3859) presented a new analysis method of nonlinear stress-strain behaviors for crystalline polymers such as polypropylene and polyethylene. A nonlinear constitutive equation including the plastic deformation and anharmonicity terms of the spring was proposed [7]. In order to characterize quantitatively the nonlinear viscoelasticity using this constitutive equation, data on the transient moduli during elongation at a constant rate of elongation are required. Then, the simultaneous measurements of linear oscillatory viscoelastic moduli during a constant rate of elongation were carried out. The plastic deformation fraction and the Grüneisen constant for crystalline polymers could be determined on the basis of the proposed method. The theoretical relaxation modulus was calculated from the constitutive equation and was compared with the experimental one under various strain levels. The agreement between experimental and theoretical curves was fairly excellent, indicating that the use of the present equation made it possible to describe the stress relaxation behavior in a nonlinear viscoelastic region.

3. STRUCTURE AND PROPERTY RELATIONSHIPS

E. Ito *et al.* (3895) studied the dielectric β-relaxation processes for a series of ethylene terephthalate/*p*-hydroxybenzoic acid (ET/PHB) copolymers with different PHB contents. The copolymers with the PHB content lower than 30% were in an isotropic amorphous glass phase at room temperature, while those with higher PHB contents were in a liquid crystalline glass phase. The latter exhibited a larger dielectric relaxation strength than the former. This result can be fully explained in consideration of the terms of the difference in the correlation length of torsional vibration of the main chains and the orientation distribution of the main chains to the electric field direction. To confirm this explanation, the dielectric relaxation measurements were carried out for the two films in which the main chain was parallel and perpendicular to the film surface. These films were prepared by molding under application of magnetic field. The orientation direction of the main chain was determined by wide angle X-ray diffraction (WAXD) measurement. The dielectric relaxation strength for the film with parallel orientation was larger than that with the perpendicular orientation. The difference in dielectric relaxation strength was well described in terms of the difference in orientation of dipole moment.

K. Kato, J. Yonezawa *et al.* (3857) studied the structure-property relationships of 1,3-cyclohexadiene (CHD)-butadiene (BD)-1,3-cyclohexadiene triblock copolymers prepared by a living anionic polymerization with an alkyllithium/amine system. The dilithium initiator with sec.-butyl group was used to obtain a narrower molecular weight distribution than that with tert-butyl one. The selective hydrogenation of PBD part of PCHD-PBD-PCHD was carried out to give PCHD-HPBD-PCHD. DSC measurement and transmission electron microscopic observation of the PCHD-HPBD-PCHD diblock copolymer film revealed the formation of microphase-separated structure. PCHD-HPBD-PCHD block copolymer showed higher mechanical strength than PS-HPBD-PS. This might be attributed to the higher cohesive energy of PCHD than PS. The large cohesive energy of PCHD induced a higher *Tg* of hard segment of PCHD-HPBD-PCHD compared with that of PS-HPBD-PS.

4. HIGH-STRENGTH FIBERS

K. Nakamae, T. Nishino *et al.* (3871) studied the temperature dependences of the elastic modulus E_l of the crystalline regions for poly(butylene naphthalate) (PBN) in the direction parallel to the chain axis on the basis of X-ray diffraction. The E_l value of PBN was 67 GPa at room temperature and 33 GPa at 353 K. Relationship between the E_l and the contraction from the planar zigzag conformation was obtained for various aromatic polyesters. The crystalline elastic modulus decreased with an increase in magnitude of contraction. The thermal expansion coefficient of the crystal lattice in the direction parallel to the chain axis also changed at around 353 K, maybe due to the thermally excited molecular motion.

T. Kunugi *et al.* (3851) applied a high-temperature drawn method in hot air to poly(ethylene-2,6-naphthalate) fibers in order to improve their mechanical properties. The drawn PEN was prepared at drawing temperature of 423 – 523 K under an applied tension of 8.7 – 17.4 MPa. The drawing ratio increased with an increase in drawing temperature and applied tension. The maximum birefringence and the degree of crystallinity at the draw ratio of 7.8 were 0.436 and 44.9%, respectively. The WAXD pattern of high-temperature hot air drawn PEN showed only α-form crystal. The tensile modulus of high-temperature hot air drawn PEN was 29.6 GPa, being comparable to the magnitude for the sample prepared by zone-drawing/zone-annealing method. The temperature dependence of dynamic viscoelasticity showed that the α-absorption temperature shifted to higher temperature region with an increase in applied tension. This result indicates an effective restriction of thermal molecular motion in an amorphous phase with an increase of drawing ratio.

References

[1] Saruyama, Y. (1986). *Thermochim. Acta*, **283**, 157.
[2] Morikawa, J., Tan, J. and Hashimoto, T. (1995). *Polymer*, **36**, 4439.
[3] Yamamoto, T. and Nozaki, K. (1997). *Polymer*, **38**, 2463.
[4] Kajiyama, T., Tanaka, K., Ohki, I., Ge, S.-R., Yoon, J.-S. and Takahara, A. (1994). *Macromolecules*, **27**, 7932.
[5] Kajiyama, T., Tanaka, K., Satomi, N. and Takahara, A. (1998). *Macromolecules*, **31**, 5150.
[6] Nitta, K., Suzuki, K. and Yamaguchi, M. (1997). *Rept. Progr. Polym. Phys., Japan*, **40**, 333.